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The Influence of Mechanical Activation on Sintering Process of BaCO₃-SrCO₃-TiO₂ System

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Abstract:

In this article the influence of mechanical activation on sintering process of barium-strontium-titanate ceramics has been investigated. Both non-activated and mixtures treated in a planetary ball mill for 5, 10, 20, 40, 80 and 120 minutes were sintered at 1100-1400 °C for 2 hours in presence of air atmosphere. The influence of mechanical activation on phase composition and crystal structure has been analyzed by XRD, while the effect of activation and sintering process on microstructure was investigated by scanning electron microscopy. It has been established that temperature of 1100 °C was too low to induce final sintering stage for this system. Electrical measurements have been conducted for the densest ceramics sintered at 1400 °C for 2 hours.

Keywords: Mechanical activation, Sintering, SEM, Crystal structure, Barium-strontium-titanate.

1. Introduction

Ba_{1-x}Sr_xTiO₃ (BST) is a continuous solid solution between two traditional ferroelectrics - barium titanate (BaTiO₃) and strontium titanate (SrTiO₃). The Curie temperature of BST decreases linearly with increasing Sr concentration at a rate of 3.4° C per mole % Sr. Therefore BST's Curie temperature and its properties can be tailored over a wide range to meet the requirements of different applications [1]. This kind of flexibility in properties and the potential application range is absent in conventional ferroelectric ceramics. Within the so-called electronic ceramic (insulator, thermistor, electro-optic, piezoelectric ceramics, memory devices based on ferroelectric ceramics, etc.) ceramics-based BST and other compounds with the perovskite structures is of particular interest given the possibility of design and development of new electronic components [2-9].

Ferroelectric materials with perovskite structure are an important set of multifunctional materials that are widely used in modern electrical engineering and electronics, such as multilayered ceramic capacitors of high capacitance, electro-optical

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devices, ferroelectric memories and pyroelectric sensors being consequently the subject of numerous researches. Miniaturization of electronic devices requires synthesis of nanoscaled ferroelectric structures which have their properties changed significantly. These structures are interesting because of the piezoelectric properties, i.e. miniaturization of piezoelectric sensors, which are used for example in medicine and ultrasonic devices, then in development of adjustable components for radio and microwave frequencies, etc.

Barium-strontium-titanate (BST) is a ferroelectric material that provides great opportunities in making the adjustable components for radio (RF) and microwave frequencies (e.g., adjustable filters, phase shifters, etc.). BST dielectric permittivity can be changed by altering the electric field in which the dielectric is positioned. Plate capacitor changes greater than 50 % can be achieved at low voltage values, 2 to 5 V. By changing the film thickness a wide range of operating voltages are attainable. Great BST dielectric permittivity (about 300 at room temperature) allows creation of capacitors of large capacity [10].

Besides this, in temperature range in which a ferroelectric behaviour is conditioned, the properties of these materials are changing depending on the ratio of Ba and Sr. For example, the pore size increases while shift of Curie point (TC) in the direction of lower values is observed with increment of Sr content according to equation $T = 127.4 + 331 \cdot x$. Dielectric constant, ϵ_r , is significantly lower in samples with a higher concentration of Ba ($x = 0.25, 0.35, 0.40$), while the existence of the dielectric constant in ferroelectric stage with sample $x \leq 0.35$ cannot be measured in microwave domain at room temperature. With the increase of the Sr content the temperature transition decreases, while the density of the sample decreases linearly. The grain size (μm) increases with sintering temperature for samples with a higher concentration of Ba. In our research, the influence of mechanical activation on the sintering process of $\text{BaCO}_3\text{-SrCO}_3\text{-TiO}_2$ system has been investigated.

2. Experimental procedures

For the experimental research of the influence of mechanical activation on sintering of the $\text{BaCO}_3\text{-SrCO}_3\text{-TiO}_2$ system, in this study powders of BaCO_3 (99.8% and Aldrich), SrCO_3 (99.8% and Aldrich) and TiO_2 (99.99% and Aldrich) were used. Initial samples were milled in 500 cm^3 zirconium oxide beakers together with balls of 10 mm diameter (the ratio of powder and ball was 1:20). Samples of activated and then calcined BST powders were pressed at 4 t/cm^2 (392 MPa) and sintered in presence of air atmosphere and in lab chamber furnaces (Electron) which maximum temperature is 1600 °C. Pressed samples were placed in alumina containers and in amount of 4 samples for each temperature and time. At that point the samples were introduced into the furnace and sintered at temperatures of 1100, 1200, 1300 and 1400 °C. Heating rate was 10 °C/min, and when the furnace reached temperatures of 1100, 1200, 1300 and 1400 °C, the pressed samples were sintered isothermally for 0, 5, 10, 20, 80 and 120 minutes in presence of air atmosphere. Tests of micro-structural properties of sintered BST were performed on Scanning electron microscope (SEM, JSM-6390 LV JEOL, 25kV).

Screening of X-ray diffractograms of the sintered samples was done at room temperature, by using the Bragg-Brentano geometry, the device Philips PW 1050, using the $\lambda\text{CuK}\alpha$ radiation and the "step scan" mode with increments of 0.05°. In addition to sintered samples, calcified samples were recorded on the same machine but under different conditions. The intensity of diffraction rays is recorded in range of angles 2θ (10-135), in the "step scan" mode with steps of 0.02 and retention of detectors of 15 s per step.

Recording of electrical characteristics of non-activated and mechanically activated BST sintered at 1400 °C (BST-S-0, BST-S-5, BST-S-10, BST-S-20, BST-S-80 and BST-S-120) has been done. Measurements of dependence of ϵ_r (T) were carried out on device HIOKI 3532-50 LCR HiTESTER, at operating frequency of 1 kHz. Sample preparation involved the

application of platinum paste on both sides of sintered samples, which were then heated for 30 minutes at 150 °C with the intent of curing paste and improving conductivity.

3. Results and Discussion

One of the most important technological procedures used for the synthesis of advanced materials, which provides the possibility of obtaining materials with predefined properties, certainly is the sintering process [11]. Changes in the size and structure of the particles during mechanical activation lead to morphological and structural instability of starting powders, which is reflected in the changed sinterability of corresponding compact samples, at a given sintering regime, and therefore changes in their final structure. During mechanical activation the microstructure of the starting powders is changing, becoming more dispersive and defective with the extension of activation time. In the case of mechanically activated BST various phenomena related to the activated sintering could be expected, too. The thickening flow could be followed through changes in relative density, porosity, volumetric and linear shrinkage, or through some relationships that connect home sintered density with theoretical density [12]. We have carefully examined the relative density and porosity. Density of the samples was determined by calculation comparing measurements of the mass and dimensions of the samples. Theoretical density (TG) of the powder BST is 5.838 g/cm³. The value of the theoretical density is taken from the JCPDS card (International Centre for Diffraction Data).

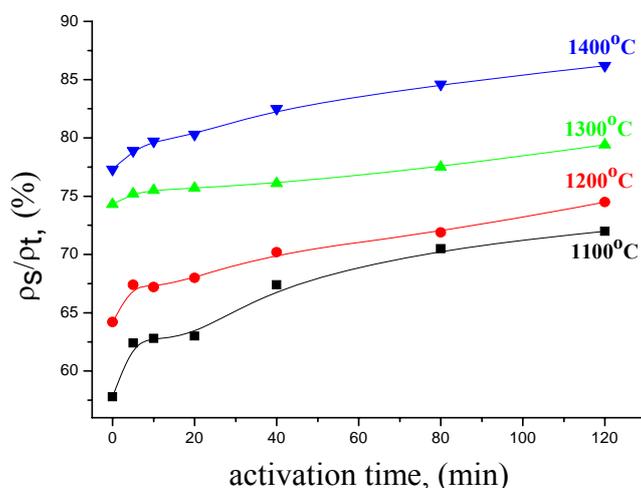


Fig. 1. Relative density in the dependence of activation time of BST-S sintered for 2 h at 1100, 1200, 1300 and 1400 °C.

Fig. 1. presents a graph of the relative density achieved by sintering, depending on the sintering time and temperature range. The highest density variation takes place up to 20 minutes for activation of powders sintered at 1100 and 1200 °C 2 hours. Density of mixture of all powders of BST increases with temperature and sintering time and reaches its maximum of 86.2 % of TG mixture BST-S-120 sintered at 1400 °C. Saturation curve clearly indicates that the sintering process has entered the final phase for the samples sintered at higher temperatures.

Diffraction patterns of sintered samples of no-activated BST and mechanically activated for 120 minutes at 1400 °C (BST-S-0 and BST-S-120) are shown in Fig. 2.

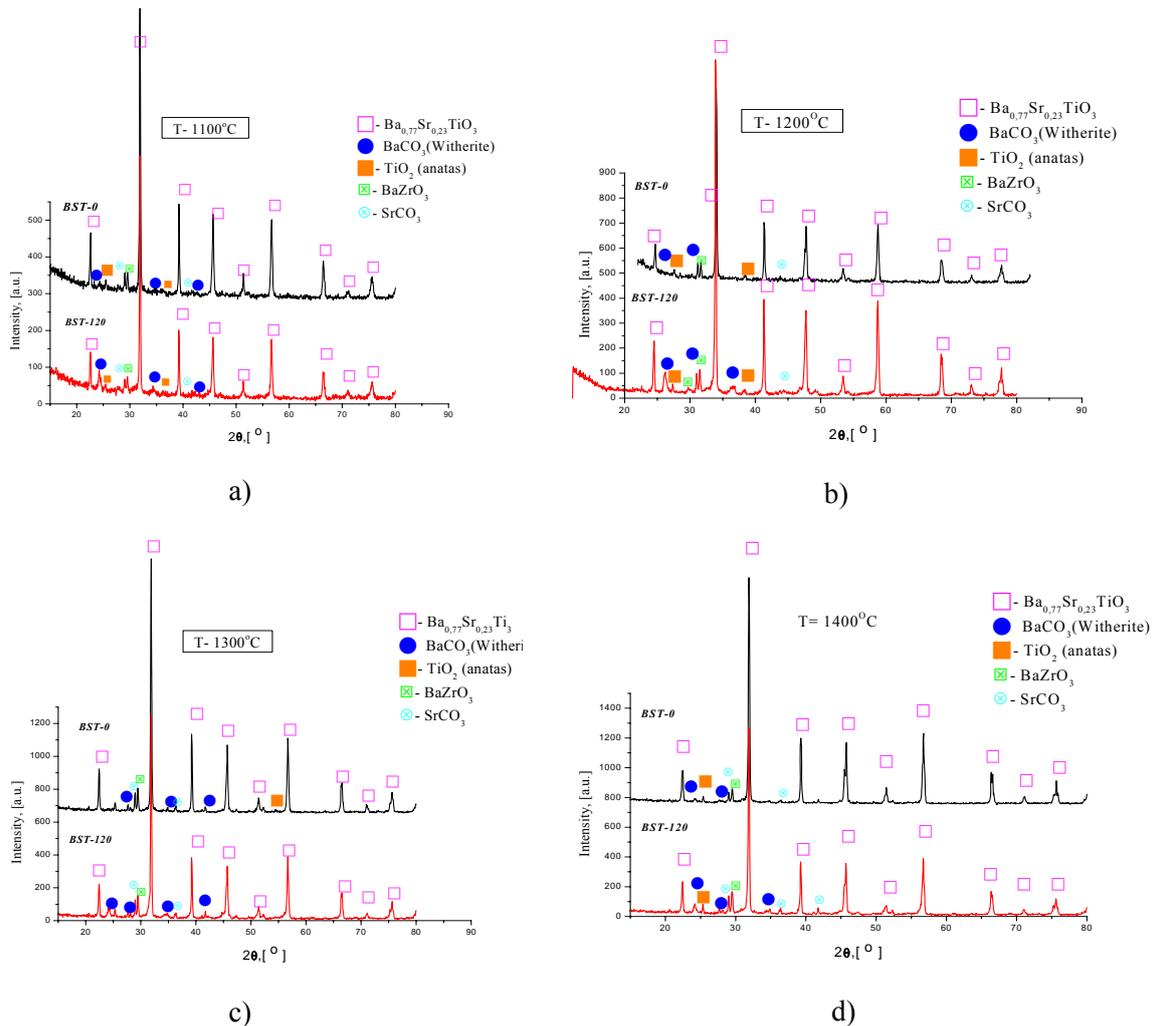


Fig. 2. Diffraction patterns of sintered BST-S-0 and BST-S-120 at 1100, 1200, 1300 and 1400 °C.

Diffraction patterns clearly indicate that the phase composition of the sintered samples is actually made up of five phases. Well-crystallized phases $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$ was detected in all sintered samples with clear presence of the strongest diffraction lines, and other phases that are present in low concentrations, such as: witherite (BaCO_3), strontium-carbonate (SrCO_3), anatase (TiO_2) and barium-zirconium oxide (BaZrO_3). Identification of the reflections was carried out using the FIND IT and ICSD (Inorganic Crystal Structure Data) and JCPDS (Joint Committee on Powder Diffraction Standards) cards. It was concluded that this was a tetragonal structure (JCPDS Card. No. 44-0093, ICSD Card. No. 54150). Diffraction patterns show sharp and intense reflections of barium-strontium-titanate due to re-crystallisation which occurs during sintering process. It suggests that this is actually a reaction sintering, because the sintering and reaction occurs in the solid phase, which means we got the final stage - the product. In addition, the peaks of sintered samples are reduced with milling time, which means that there is narrowing of the reflection or improvement of crystallinity of material samples. Knowing that an increase in the sintering temperature stabilizes the crystal structure precisely because of the re-crystallization process, all of these facts unambiguously lead to the conclusion that in our system, actually, the solid solution of composition ($\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$) has been formed.

From the diagram of the samples sintered at 1100 °C reflection (111) was selected because it is not overlapping with any other reflection. This reflection is fitted with functional profile (Fullprof) in order to determine the full width at half-height (ISQ FWHM - "full width at half-maximum") and the results are shown in Fig. 3.

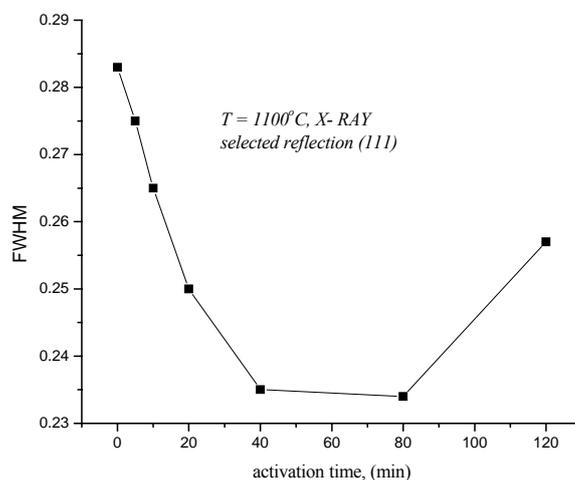


Fig. 3. Effect of time of mechanical activation of samples sintered BST-S on change of width at half height of diffraction lines (111) (done by fitting the budget line (111)).

From Fig. 3. it is obvious that increase of milling time leads to the decrease in FWHM diffraction lines, which means that there is a narrowing of reflections (111), i.e. improvement of the crystallinity of the material for samples mechanically activated for up to 80 minutes. Furthermore, reduction of the value of FWHM diffraction pattern lines derives from reductions of micro-strains within the grid and/or increase in size of the crystallites. With the BST sample mechanically activated for 120 minutes, a spread of reflection i.e. demolition of the structure during milling occurs, which is observed by a sharp increase in FWHM. This expansion of peaks, i.e. demolition of the structure, is also proof of increase of micro-strain and/or a reduction in the average crystallite size.

Micrographs of the samples of BST-S-0, BST-S-5, BST-S-10, BST-S-20, BST-S-80 and BST-S-120 sintered at 1400 °C non-isothermally, and for two hours at this temperature isothermally, are shown in Fig. 4. For the microstructure of ceramic materials, in general, it could be said to consist of two phases: material phase and pore phases. During the sintering, process leads to the evolution of micro-structural constituents, grains and pores, while with increase of sintering time appropriate processes of grain growth and reduction of the pore size are taking place. With analyses of SEM micrographs of samples BST-S-0 and BST-S-5, Fig. 4. (a) and (b) it becomes noticeable that the structure of each sample is characterized by high open (BST-S-0) and closed (BST-S-5) porosity of grains of different sizes. Micrographs of sintered sample BST-S-0 and BST-S-5, indicate the presence of larger, well-formed grains of barium-strontium-titanate (as one phase) and smaller grains along the edges of larger build-up (as of the second phase). What's more, with non-activated samples and samples mechanically activated for five minutes, it was determined that inhomogeneous porous microstructure is being formed, in which polygonal grain shape prevails, as well as the presence of so-called textural open porosity [13] with pores of irregular shape. With samples mechanically activated for 10 and 20 minutes densification and uneven grain growth (barium-strontium-titanate) is evident (Fig. 4. (c) and (d)). Micrographs revealed the presence of second phase particles (smaller particles), which are somewhat more uniformly distributed. Also, with

samples that were mechanically activated 10 and 20 minutes the increased mass transport has been found, caused by higher surface activity of grain boundaries, which leads to their structural reinforcement, resulting in fracture patterns. From micrographs shown in (Fig. 4 (e) and (f)) it is evident that with the increase of a activation time the growth of the new phase is more even, while the size of the second stage has been reduced while boundaries between the grains are strengthened. This all leads to creation of the most compact structure of a polygonal shape that is medium sized with a slight presence non-reacted second stage. Besides, there is dominant presence of closed porosity in which sphere appearance of pores was identified, and this phenomenon shows that this system has entered the final stage of sintering. Generally it can be said that with the increase of activation time, the change in size and shape of the particles, as well as the type of porosity, is evident.

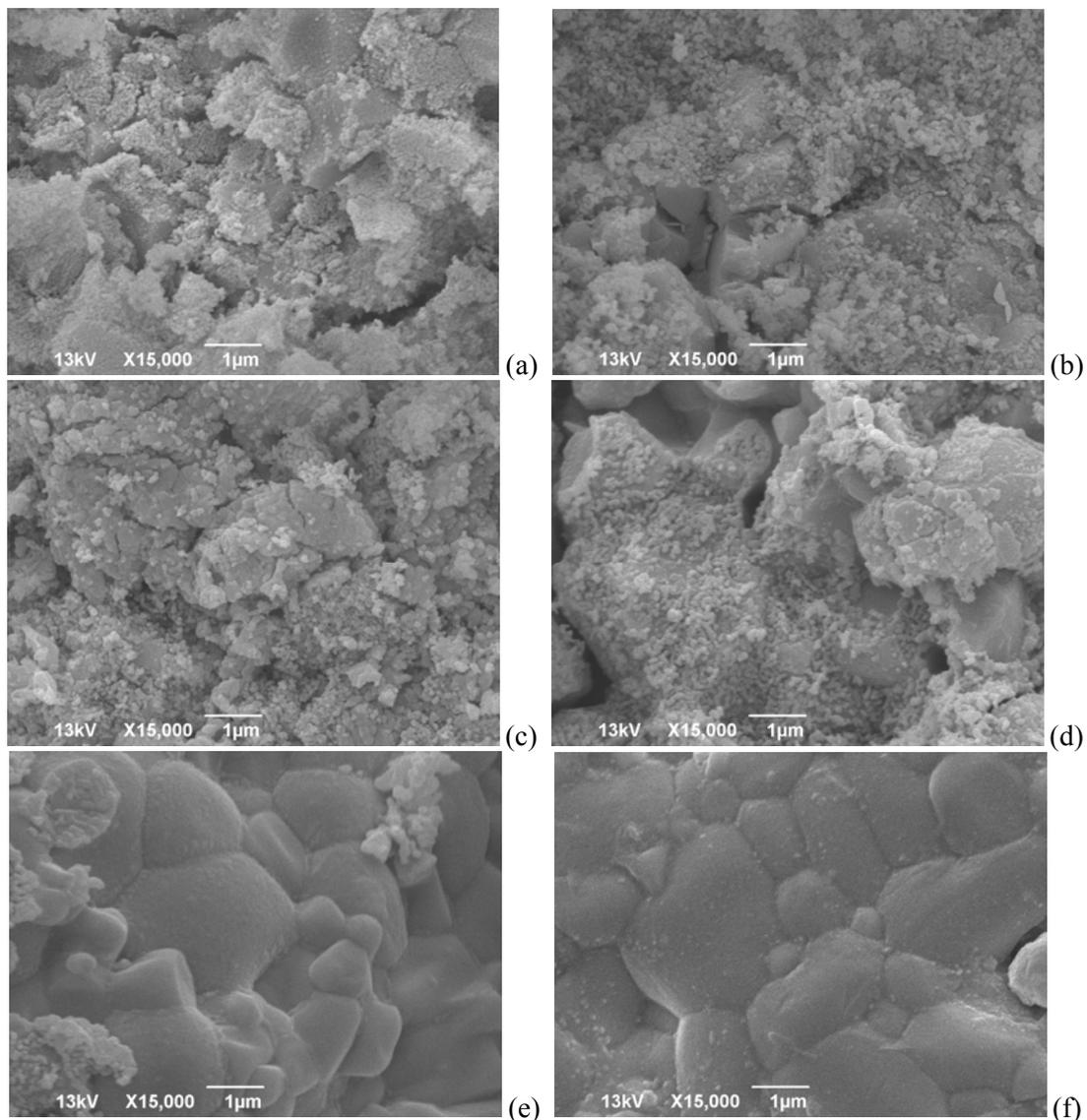


Fig. 4. Scanning electron micrographs of samples a) BST-S-0, b) BST-S-5, c) BST-S-10, BST-S-20, BST-S-80 f) BST-S-120 sintered non-isothermally on 1400 °C and for two hours isothermally.

Activation influence on the temperature dependence of the relative dielectric permeability of sintered samples $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_2$ (BST) at 1400 °C is considered at a frequency of 1 kHz and presented in Fig. 5.

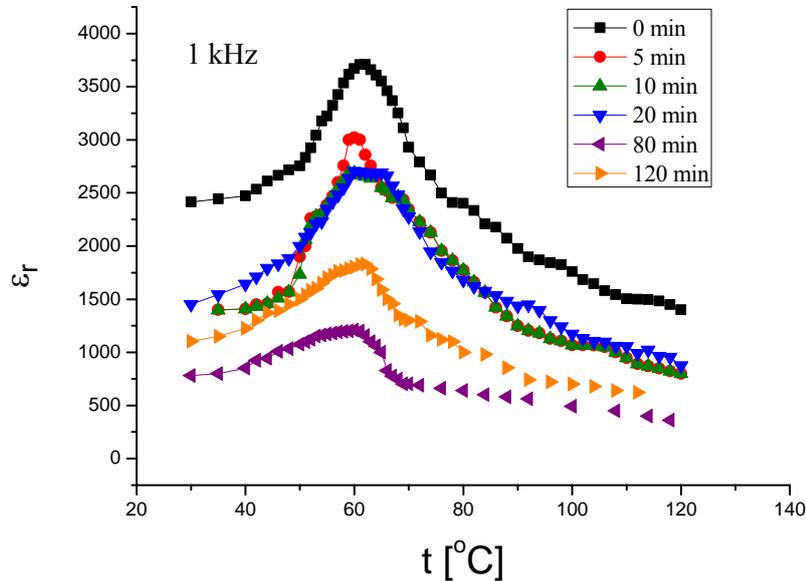


Fig. 5. Influence of activation time on the graph by temperature dependence of real component of relative dielectric permeability of the BST at a frequency of 1 kHz.

With the increase in the activation time to 80 min, on the graphics $\epsilon_r = f(t)$ is observed: the decline of the value of the dielectric permeability ϵ_r max, the increase in ϵ_r ferroelectric phase for the shortest activated samples and declining values of ϵ_r (Fig. 5 and Table I). It was also noted that activation of the precursor powder leads to a decrease in Curie-point (T_C) in the sintered samples and to the spread of spades on the diagram of temperature dependences $\epsilon_r = f(t)$, compared to the inactivated samples (Fig. 5. and Table I). Based on literature data on the influence of the crystallite size in ferroelectric ceramics value ϵ_r max, Curie-point and width (sharpness) peak in the diagram of depending $\epsilon_r = f(t)$ [14,15], it can be concluded for samples in which the X-ray analysis also found that the reaction of synthesis of tetragonal $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$ (BST) happened at the end, or at the stage in which the presence of residual inter-medial phase is negligible. A decline in the value of T_C can be considered as a result of the influence of changes in the size of BST-crystallites in these samples, and related values in the internal micro-strain, with increasing activation time [16].

Tab. I. Influence of activation time on change: the values of ϵ_r max on graphics of dependency $\epsilon_r = f(t)$, values of $\text{tg}\delta$ on graphics of decency $\text{tg}\delta = f(t)$, the temperatures values for which and $\text{tg}\delta$ reaches a maximum (T_C). Given measurements were performed at a frequency of 1 kHz.

| Activation [min] | 1 kHz | | 1 kHz | |
|------------------|-------------|-----------------------|-------------|-------------------|
| | T_C [°C]* | $\epsilon_{r \max}^*$ | T_C [°C]* | $\text{tg}\delta$ |
| 0 | 62 | 3710 | 60 | 0.1463 |
| 5 | 60 | 3021 | 60 | 0.1336 |
| 10 | 60 | 2690 | 60 | 0.1919 |
| 20 | 60 | 2705 | 60 | 0.1000 |
| 80 | 60 | 1209 | 58 | 0.0920 |
| 120 | 62 | 1380 | 64 | 0.1195 |

* $\Delta T = \pm 1^\circ\text{C}$; $\Delta \epsilon_{r \max} = \pm 10$

Although within the starting powders with increasing activation time (t_A) non-agglomerated particles reduce the size, the occurrence of secondary agglomeration of powder activated during $t_A \geq 10$ min affects the final structure and properties of sintered samples. Bearing in mind that the literature data shows that agglomeration of barium-strontium-titanate nanoparticles favour the tetragonal phase in the powder [17], it is assumed that in our research, secondary agglomeration in the starting powders with those ≥ 10 min influences that further decline of T_C values in the sintered samples obtained from these powders, can not be seen, as compared to the samples with activation of 5 min (Table I).

From Fig. 5. it can be further noted that the activation of 120 min leads to a reverse trend in behavior of materials in relation to the behavior with increased activation time to 80 minutes. Then, there is an increase in the value of ϵ_r max, a slight increase in T_C and narrowing of peaks in relation to the rest of the activation time. Therefore, the form graph of temperature dependence $\epsilon_r = f(t)$ for activation of 120 minutes at most resembles the graph of non-activated samples. Based on these results it can be concluded that the specific structural characteristics of the starting powder activated for more than 80 minutes, which are derived from the process of dynamic recrystallization during mechanical activation, clearly reflected on the electrical properties of the sintered samples.

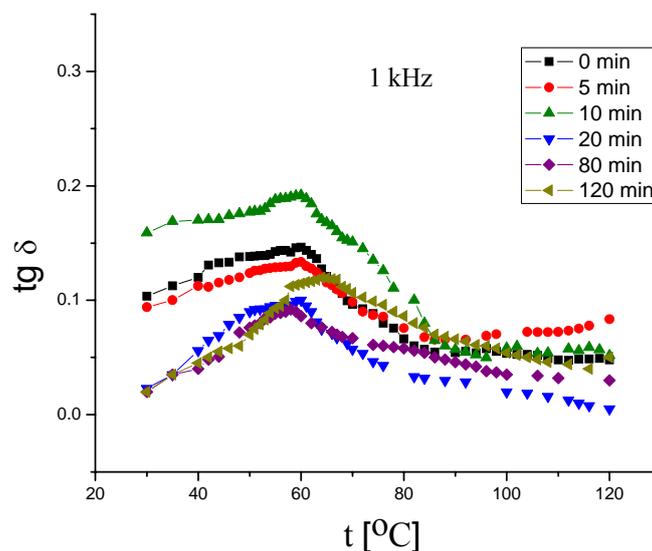


Fig. 6. Influence of activation time on the graph of temperature dependence of dielectric losses in BST sintered at $\nu = 1$ kHz.

Analysis of the influence of mechanical activation on temperature dependence of the dielectric loss at a frequency of 1 kHz was based on a diagram $\text{tg}\delta = f(t)$ (Fig. 6). This function shows a peak in the Curie-point, and based on the graphics shown in Fig. 6. it can be concluded that $\text{tg}\delta$ (T_C) increases with increasing sintering temperature, i.e., the peaks were more pronounced. It was observed that in all sintered samples during the increase of time of activation, first the decline in the value of Curie-point occurs, and then possibly decline in the value $\text{tg}\delta$.

4. Conclusion

In this article, the influence of mechanical activation on the sintering process $\text{BaCO}_3\text{-SrCO}_3\text{-TiO}_2$ is researched. Based on measurements of the relative density of the sintered BST

samples at 1100, 1200, 1300 and 1400 °C, we concluded that the greatest density variation occurs up to 20 minutes of mechanical activation of powders sintered at 1100 and 1200 °C. Based on these results, we have also found that the density of BST samples increased with sintering temperature and time, and reached its maximum of 86.2 % TG at a temperature of 1400 °C. The diffraction patterns clearly indicate the phase composition of the sintered samples is actually made up of five phases: $Ba_{0.77}Sr_{0.23}TiO_3$ which was detected in all sintered samples, then witherite ($BaCO_3$), strontium-carbonate ($SrCO_3$), anatase (TiO_2) and barium-zirconium oxide ($BaZrO_3$). The diffraction patterns show sharp and intense reflections of barium-strontium-titanate due to recrystallisation which occurs during sintering, and suggest that this is actually a reaction sintering. Peaks of sintered samples with milling time are reduced, which means that there is a narrowing of the reflections i.e. improvement in crystallinity of material samples, based on which we can conclude that in our system actually firm solid solution, composition ($Ba_{0.77}Sr_{0.23}TiO_3$) is formed.

With SEM analysis it is demonstrated that presence of a uniform material densification occurs with increase of mechanical activation. Also, the dominant presence of closed porosity in which sphere appearance of pores was identified and this phenomenon shows that the system has entered the final stage of sintering. Generally it can be said that with the increasing time of activation, change in the size and shape of the particles happened, as well as the type of porosity, which confirms the results obtained by X-ray analysis.

By studying electrical properties of sintered $Ba_{0.77}Sr_{0.23}TiO_3$ samples, it was concluded that as the dominant influence of mechanical activation performed for 5-80 minutes, the decline of the values of dielectric permeability of ϵ_r max and loss tangent $tg\delta$ can be extracted, as well as the increase in ϵ_r ferroelectric phase for the shortest activated samples and declining of values of ϵ_r and $tg\delta$. We also concluded that activation of the precursor powder results in a decrease of Curie-point (T_C) as well as spread of spades on the diagram by temperature dependence $\epsilon_r = f(t)$, compared to the inactivated samples.

Acknowledgements

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Садржај: У овом раду проучаван је утицај механичке активације на процес синтеровања баријум-стронцијум-титанатне керамике. Неактивирана и механички акативирани смеше (у температурском интервалу 5 - 120 минута) у високо-енергетском планетарном млину синтероване су на 1100 - 1400 °C два сата у атмосфери ваздуха. Утицај механичке активације на фазни састав и кристалну структуру је анализиран помоћу рендгенске дифракције, док је дефекат активације и процес синтеровања на микроструктуру испитиван скенирајућом електронском микроскопијом. Утврђено је да је температура од 1100 °C била исувише ниска да се подстакне завршна фаза синтеровања за овај систем. Електрична мерења су спроведена за најгушће керамике синтероване на 1400 °C два сата.

Кључне речи: Механичка активација, синтеровање, скенирајућа електронске микроскопија, кристална структура, баријум-стронцијум-титанат.
